Energy, Mines and Resources Canada

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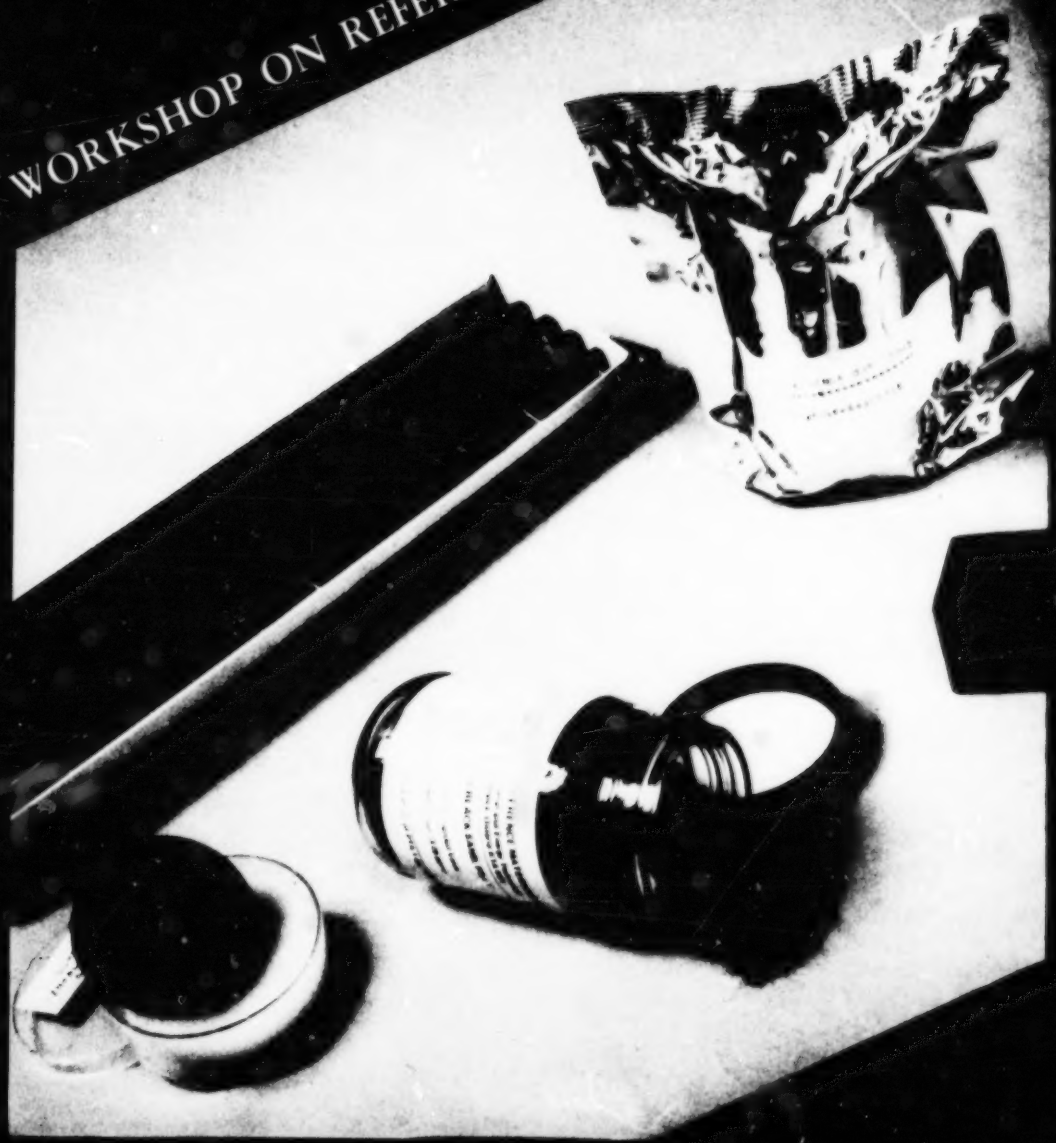
WORKSHOP ON REFERENCE MATERIALS



CANADIAN CERTIFIED REFERENCE MATERIALS PROJECT

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WORKSHOP

ON

REFERENCE MATERIALS

by

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46 pp

FOREWORD

It is by no means stretching the truth to surmise that nearly every analytical chemist regardless of his area of expertise uses "standard samples" or reference materials, in proper terminology, either to ensure or assess the quality of his results or to verify methods. The high demand for reference materials of all types from such wide-spread use is at present being satisfied by approximately 130 producers in the western world. Even if only compositional reference materials such as ores, rocks, metal alloys, etc., are considered, the approximately 39 producers offer a sufficiently large number of reference materials not only of many varying types but also certified by different procedures or suitable for different purposes. Although reference material producers are cooperating through REMCO, the Council Committee on Reference Materials, for ISO, the International Organization for Standarization, to bring about uniformity in the preparation, certification and use of reference materials, the "nature of the beast" does not make it possible to have a single mode of certification or of use. It is important therefore that the analyst be able to select the reference material that is most appropriate with respect to the certified chemical constituents and overall chemical composition as well as to intended use.

As part of the START Program of the Office of Technology Transfer of CANMET, the Canadian Certified Reference Materials Project (CCRMP) is offering an information workshop on reference materials in several centres in or near high mining or analytical activity in Canada. This workshop consists of four oral presentations on the available reference materials of CCRMP, the modes and uses of reference materials and international cooperation in reference materials. Its aim is to help analytical chemists, not only heads of laboratories but especially those working at the bench, to become more aware of the wide availability of reference materials and also to realize the need for the proper selection and appropriate use of such reference materials. It is hoped to foster an increased use of reference materials, thereby improving the quality of the analytical output of Canadian laboratories.

This compilation of the presentations is intended to make such information on reference materials available to those analysts that are unable to attend the workshops.

AVANT-PROPOS

Nous croyons assurément ne pas exagérer en supposant que presque tous les chimistes en chimie analytique utilisent des "échantillons types", ou, en termes techniques, des matériaux de référence, et cela quel que soit leur domaine de compétences, afin d'évaluer ou de s'assurer de la qualité de leurs résultats ou pour vérifier leurs méthodes. Actuellement, environ 130 producteurs dans le monde occidental répondent à la vaste demande de matériaux de référence de tous types, pour des usages très variés. Même si l'on ne considère que les matériaux de référence de composition comme les minerais, les roches, les alliages de métaux etc., les quelque 39 producteurs intéressés offrent une quantité suffisante de matériaux de référence, non seulement de plusieurs types différents, mais aussi qui ont été homologués selon différents procédés, et pour des usages divers. Bien que les producteurs de matériaux de référence prêtent leur collaboration par l'intermédiaire de REMCO, le Comité consultatif sur les matériaux de référence de l'ISO, l'Organisation internationale de normalisation, pour offrir une uniformité de préparation, d'homologation et d'utilisation des matériaux de référence, la nature même de ces matériaux ne permet pas un seul mode d'homologation ni d'utilisation. Il est donc d'importance capitale que l'analyste puisse choisir les matériaux de référence convenant le mieux aux constituants chimiques homologués et à la composition chimique globale, ainsi qu'à l'usage qu'on lui réserve.

Dans le cadre du programme START de Bureau de transfert de la technologie du CANMET, le Projet canadien des matériaux de référence (CCRMP) offre un atelier d'information sur les matériaux de référence dans divers centres de grande activité minière ou analytique au Canada, ou près de ces derniers. Cet atelier se compose de quatre présentations orales sur les matériaux de référence disponibles au CCRMP, ainsi que sur leurs modes et usages, et la coopération internationale s'y rapportant. Le but de cet atelier est d'aider les spécialistes de la chimie analytique, non seulement les chefs de laboratoires mais aussi ceux qui travaillent au banc, à devenir plus conscients de la grande disponibilité des matériaux de référence, de meme que du besoin de leur choix et de leur usage appropriés. Nous expérons encourager un usage accru des matériaux de référence, et améliorer de ce fait la qualité des analyses provenant des laboratoires canadiens.

Ce recueil de présentations est destiné à rendre les renseignements disponibles à tous les analystes qui ne pourront prendre part à l'atelier.

THE CANADIAN CERTIFIED REFERENCE MATERIALS PROJECT

by

H.F. Steger

HIGHLIGHT

The goal of the Canadian Certified Reference Materials Project (CCRMP) is to prepare certified compositional ores, concentrates and related products that are of Canadian origin and not in general available elsewhere for use in analytical laboratories associated with mining, metallurgy and the earth sciences. To date, CCRMP has certified 46 such reference materials (for a broad range of elements) that are used by approximately 850 laboratories in 50 countries.

This presentation touches upon the importance of the measurement process in commerce and on the role of reference materials in measurement in analytical laboratories. The certification procedures of CCRMP are described. Finally, the contribution of CCRMP to the analytical community is discussed with respect to the number of and wide range in the nature of reference materials available from CCRMP. The uniqueness of CCRMP as a reference material preparation facility for out-of-CANMET organizations is demonstrated.

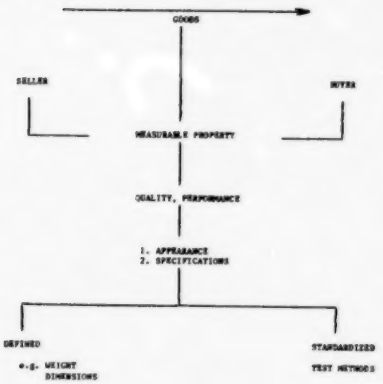
THE CANADIAN CERTIFIED REFERENCE MATERIALS PROJECT

by

H.F. Steger

Before I commence to describe the Canadian Certified Reference Materials Project, which I will refer to hereafter as CCRMP, I would like to discuss very briefly why reference materials (RMs) are necessary.

REFERENCE MATERIALS — WHY?



The smooth exchange of goods whether between individuals, companies or nations proceeds only if there is agreement on some property related to quality, performance, etc., of these goods by both the buyer and the seller. The measurement of this property may be relatively simple such as a subjective assessment of the physical appearance. For example, someone seeking marble chips for decorative purposes is not concerned with exact chemical composition. Rather he is concerned that the colour meets his requirement. The measurement of this property of the goods can however be more exacting and require compliance to specifications. Often these specifications are contextual with standardized test methods. For example, a buyer of iron ore may specify a minimum iron content. If the buyer and the seller agree on the iron content even though obtained by different methods, the transaction is completed. However, where the buyer and seller seriously disagree about the iron content or where the iron content is close to the acceptable minimum value, either party may require resolution of the dispute in the first instance or verification of the iron content in the second by a widely-accepted test method such as ISO method 585E.

Similarly, non-commercial but equally important endeavors such as the assessment or regulation of the extent of environmental pollution, the accountability of nuclear materials or the determination of biological substances would be untenable without reliable procedures of measurement.

Measurement problems encountered by analytical laboratories associated with mining, metallurgy and geochemistry are essentially addressed to chemical composition. In this instance, a consensus of measurement is best achieved through the use of a rock, ore, etc., for which the concentration of one or more elements has been well established; such a rock, ore, etc., is a RM. A certified RM is a RM accompanied by or traceable to a certification document that is issued by an organization that is widely accepted as technically competent.

The use of RMs assures the quality of data and/or consensus in these data among analytical laboratories by:

- the direct calibration of methods and instruments
- the verification of precision, accuracy and sensitivity of methods used in process control, and
- the evaluation and development of new or reference methods.

In addition, the use of RMs as unidentified check samples included in a series of real samples serves to measure the overall quality of the analytical results.

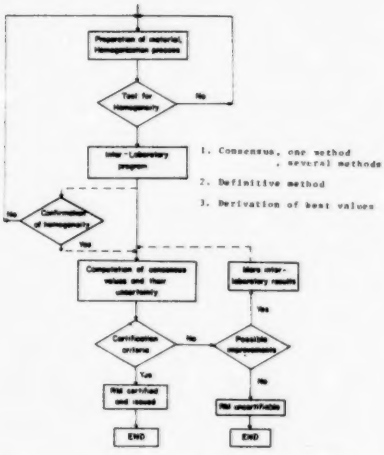
CCRMP

CCRMP was initiated as an authorized entity of CANMET approximately a decade ago. It had its beginning in the Copper and Copper Alloy Standards Committee formed in 1955 by representatives from the Canadian metal industry and the then Bureau of Mines and Technical Surveys which subsequently became the Mines Branch and currently CANMET. The Canadian Association of Applied Spectroscopy, since renamed the Spectroscopy Society of Canada (SSC), provided some funding. This committee resulted in the release for sale in 1962 of three phosphor bronze discs certified for six elements and in 1969 of four commercial-purity copper alloy rods certified for twelve elements.

A Non-Metallic Standards Committee was established in 1957 for the preparation of standard samples for geochemistry. Subsequently, three syenites and a sulphide ore were certified.

By the mid 60's, the concept of a government agency to further the preparation of standards had materialized and, as a consequence, the Mines Branch became increasingly involved with the procurement, preparation and certification of RMs. In 1973, the Standards Committee of the Spectroscopy Society of Canada transferred all rights to previously prepared RMs to the CCRMP with the proviso of retaining representation on the Coordinating Committee responsible for the selection of RMs. The assumption of management on a program basis by CANMET in 1975 made it unfeasible for CCRMP to be under the direction of this Coordinating Committee which has however been retained in an advisory capacity.

I should now like to describe the preparation and certification procedures used in CCRMP. I will however discuss in detail only those facets which will not be covered in the following presentations. The next slide summarizes the distinctive stages leading to the certification of RMs.



Preparation of RMs

The selection of a candidate RM results from:

1) Consultations between CCRMP and potential users. Both my predecessors and myself have and will continue to visit analytical laboratories throughout Canada on a periodic basis for this purpose.

2) Unsolicited requests from out-of-CANMET organizations.

3) Advisory Committee.

4) Need to replenish the stock of certain RMs. This has become an important aspect within the last three years.

The raw material is donated by industry, mining corporations or government agencies. From time to time, material of suitable grade has been handpicked by mineralogists from both CANMET and outside. In some cases, high-grade ore and waste rock have been blended to achieve a desired concentration of selected elements.

For powdered RMs, the raw material (100 to 300 kg) is dry-ground to minus 200 mesh, mixed in a conical blender and bottled in 100 to 400 g units. Randomly selected bottles are then analyzed to confirm that it is sufficiently homogeneous for use as a RM. For metal alloys, the material as supplied by the producer is sub-divided into conveniently sized samples, i.e., discs or rods, and tested for homogeneity.

Homogeneity

The raw materials for RMs consisting of mixed powders, ores, rocks, alloys, etc., are heterogeneous by nature so that RMs must be tested to assess the degree of homogeneity. These RMs can be divided into two groups: (1) Those for which the homogeneity within each unit is subject to change, e.g., segregation of the minerals in an ore. (2) Those for which the homogeneity within each unit of packaging is fixed, e.g., solid pieces such as metal rods and discs. This group also includes powdered RMs for which segregation can occur within a unit but which are packaged in units of such size that the entire unit must be consumed. This last sub-group is often encountered among biological RMs but seldom in geochemical application.

A material is conceived to be homogeneous with respect to a given constituent if a difference between the value of this constituent from one part (e.g., bottle) to another cannot be detected. Thus the concept of homogeneity embodies a specificness to both the constituent and the determinative method employed. It is important that the method chosen to confirm the homogeneity be the most precise available. Sometimes however a compromise between the economy of time and cost must be reached.

For powdered RMs which are blended in one lot, there are basically two approaches to confirm homogeneity. In one, the candidate RM is packaged in appropriate units, generally bottles, immediately after blending. Randomly selected units are than analyzed in replicate for the constituent of interest. The within-unit variance is compared with the between-unit variance to detect a statistical significance. CCRMP currently uses this approach.

In the other, the homogeneity of RM while still in the blender is assessed. Laboratories in the round-robin certification program analyze more than one unit, usually two, of RM and the homogeneity of RM is confirmed by a series of t-tests on the results for the replicate units for each laboratory. This approach was used by CCRMP until 1981. Past experience in CCRMP and continuing experience by the South African Certified Reference Material Committee is that approximately 5 to 15% of laboratories detect a statistically significant difference between the units of RM. I personally do not believe this reflects the true homogeneity of RM. The crucial assumption in this procedure is that all laboratories treat each of the units of RM exactly the same, i.e., all or an equal number of replicate determinations from each unit are analyzed together. Any divergence from this invalidates the t-tests. CCRMP decided to abandon this procedure because such divergences occur far more commonly than is suspected.

The assessment of the homogeneity of metal alloys follows essentially the same procedure. The within-sample, e.g., disc, variance is compared with the between-sample variance to detect a statistically significant difference.

For RMs for which the entire sample has to be consumed, homogeneity is defined by the detection of a statistically significant difference between the between-sample variance and the established repeatability of the method. CCRMP does not offer this type of RM.

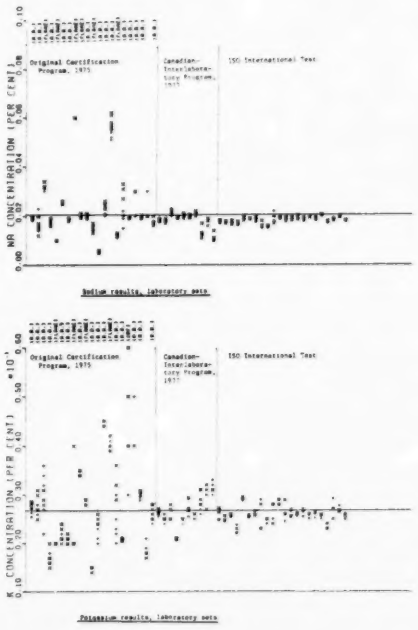
It should be pointed out that a RM confirmed to be homogeneous with respect to the

constituents of interest need not necessarily be homogeneous with respect to other constituents provided this inhomogeneity exerts no influence on the accuracy and precision of the most commonly used methods for the determination of the constituents of interest. Ideally therefore a RM should be characterized with respect to the degree of homogeneity for each constituent of interest. For RMs intended for a relatively large number of constituents, the assessment of the homogeneity for all is both economically and physically burdensome, and in some cases even unfeasible. In practice therefore, the homogeneity of only a few constituents is assessed. The constituents should be appropriately chosen on the basis of established chemical or physical relationships, e.g., an inter-element concomitance in the mineral phases of RM.

Certification of RMs

The majority of RMs of CCRMP have been certified by the consensus approach. Herein a large number of laboratories provide analytical results for a candidate RM. The overall mean is accepted as the best estimate of the true value. In one variant, one well-established, critically-evaluated method is used by all laboratories. Herein the uncertainty in the overall mean reflects the precision of the method and the between-laboratory difference. For those who are not familiar with the latter expression, the between-laboratory difference is a real, experimentally observed difference between the mean values obtained on the same material by two independent analysts, i.e., laboratories, using the same method.

The second variant is necessary where such a widely-accepted, critically-evaluated method is not available. Because this is in general the case with ores, rocks, etc., CCRMP uses a consensus approach wherein each laboratory uses the method of its choice. This scheme yields the widest uncertainty limits because they now reflect a between-method difference as well as the method precision and between-laboratory difference. This second variant however reflects the current status for the elements of interest and potentially it reveals a great deal of information on methods. Experience in CCRMP has shown that the "free-choice" scheme yields a consensus value for elements that is somewhat less precise but nearly identical to that obtained in a program wherein all participating laboratories used a "standard" method. The slide shows a comparison of the results for sodium and potassium by both variants. The wider uncertainty limits of the "free-choice" program of CCRMP compared to that of the ISO Iron Ores Working Group round-robin are evident.



I should like to point out at this time that over 170 Canadian and foreign laboratories have participated in the round-robin programs of CCRMP. Indeed the success attained by CCRMP is as much due to them as it is to in-CANMET effort.

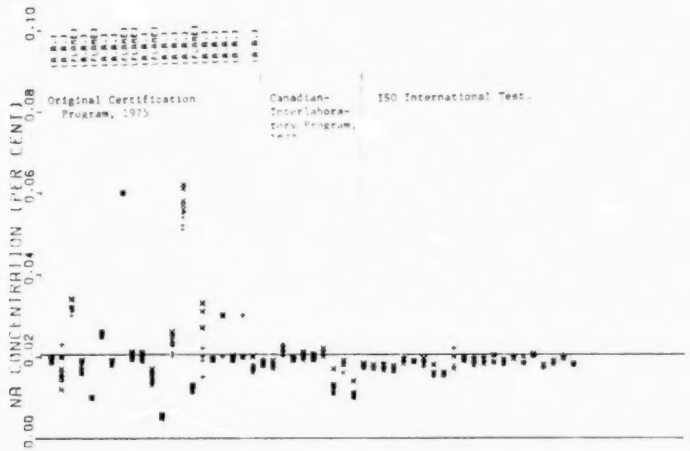
A second approach to certify a RM is the "definitive" method technique wherein the true value of the element is obtained. The uncertainty limits of this value are essentially defined by the precision of the method. This is a technique very frequently used by the National Bureau of Standards in Washington, D.C. CCRMP has itself used this approach for certifying the

uranium content of three ores, DH-1a, BL-2a and BL-4a.

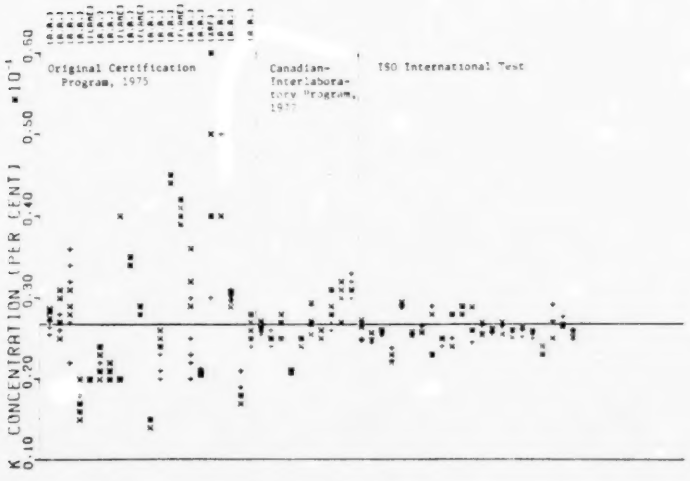
There is another approach for deriving the best value of an element in a RM - notice that I said "deriving" not "certifying". Herein the concentration of an element is estimated by a combination of statistics and analytical work experience. Often such best values are reported with questioned validity. The rock samples, SY-2, SY-3 and MRG-1, and FER-1 to -4 of CCRMP are examples of such RM's.

The mode of certification of a RM has a strong influence on the use of RM, be it for instrument calibration or titrant standardization or for verification of accuracy or precision of a method. This is however a topic I will leave for the following papers.

The next slide summarizes the stages employed in the treatment of the raw data from the round-robin program leading to the computation of the certified values. The first step is an examination of the raw data to identify and discard any results which are obviously physical outliers. Then statistical outliers are rejected; these are sets of results whose means differ by more than twice the standard deviation of the overall mean, or sets of results having unusually high variance.



Sodium results, laboratory sets



Potassium results, laboratory sets

A one-way analysis of variance technique (ANOVA) is used to estimate the consensus value and its variance. The quality of the results and of the round-robin program itself should be appraised in comparison with pre-set certification criteria. Prior to 1981, CCRMP employed the "Certification Factor" but this has now been amended to the "Rejection Percentage".

The final step is the preparation of the certification report for RM.

Sale of RMs

Most RMs are offered for sale at $35 per 100 g. Some of the more recently certified RMs may be more expensive because the round-robin certification programs were funded. In either case, the charge does not cover the real cost of preparation but is intended to discourage frivolous or unduly large orders. All revenue goes to the Receiver-General for Canada and not to CCRMP. In fiscal year 1981-82, 1531 units were sold for a revenue of $95,475, approximately two thirds of which was to foreign clients. Over 850 clients in 50 countries are or have used RMs of CCRMP.

Each order for a RM certified prior to 1979 is accompanied by a complete report on its certification. Orders for more recently certified RMs are accompanied by a Certificate of Analysis. The complete report is however available at no charge on request to the Coordinator. Interestingly, only 17 such requests have been made although over 1900 Certificates of Analysis have been issued. This clearly illustrates that analysts for the greatest part are concerned only with the certified values and not how they were derived.

RMs OF CCRMP

The establishment of a RM is an expensive, time-consuming endeavour and no one nation is capable of fulfilling the world's needs for a wide range of RMs. Consequently, most of the undustrialized nations each have programs for the preparation of RMs, essentially to meet the national demand. The goal of CCRMP is to provide compositional RMs of Canadian origin and which are generally not available from other sources for use in analytical laboratories associated with mining, metallurgy and the earth sciences. Emphasis is on the preparation of reference ores, concentrates, and related materials because of their importance in Canada's economy.

To date, CCRMP has certified 46 compositional RMs for a wide selection of elements. Most of the RMs of CCRMP can be divided into 4 groups:

1) sulphide ores and concentrates,
2) precious metal ores,
3) uranium ores and tailings, and
4) soils.

RMs presently available from CCRMP are illustrated in the next five slides. For the sulphide materials group, it is easily seen that CCRMP offers a wide selection of type of material as well as of number of elements certified. RMs other than the zinc, lead and copper concentrates are of special interest because very few such materials are available from other sources. Indeed it is safely stated that CCRMP was a pioneer in the preparation of RMs from sulphide ores and concentrates, especially those for which air oxidation can be a serious problem with respect to compositional stability. For this reason, CCRMP seals such sulphide materials under nitrogen gas in laminated foil pouches in order to extend their "shelf-life" at CANMET. Purchasers of these RMs are warned that the assigned values for the certified elements pertain to the date of issue and that CCRMP is not responsible for changes occurring after receipt by the user. These changes can be minimized by storing opened bottles under an inert gas in a dessicator or in a new heat-sealed foil pouch.

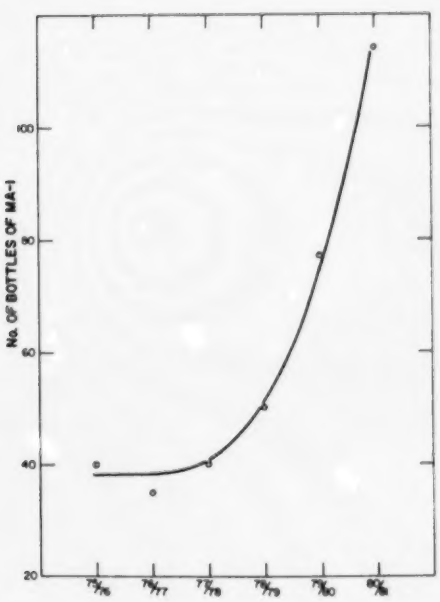
For the precious metal group, CCRMP offers five RMs. A gold tailings RM is undergoing an interlaboratory certification program this year. The only other precious metal RM that is currently available, as far as I know, is a platinum ore from SACCRM of South Africa. The trend in the sales of a particular RM is sometimes a good barometer of what is happening in the world of "real" samples from geo-exploration. As an

SULPHIDE ORES AND CONCENTRATES

RM		Certified Constituents
MP-1a	, ore	Zn, Pb, Cu, Sn, As, In, Bi, Mo, Ag
KC-1	, ore	Zn, Pb, Cu, Sn, Ag
HV-1	, ore	Cu, Mo
PR-1	, ore	Mo, Bi, Fe, S
CD-1	, ore	Sb, As
UM-1	, ore	Ni, Cu, Co
SU-1a	, ore	Ni, Cu, Co, Pd, Pt, Ag
CZN-1	, concentrate	Zn, S, Fe, Pb, Al, Mn, Co, Cd, Sb, As, Ag, Hg
CPB-1	, concentrate	Pb, S, Fe, Zn, Si, Sb, Al, Cu, As, Bi, Cd, Ag, Hg
CCU-1	, concentrate	Cu, Zn, Si, Al, Pb, Ag, Hg, Au

PRECIOUS METAL MATERIALS

RM		Certified Constituents
MA-1	, ore	Au
MA-2	, ore, waste rock	Au
PTC-1	, sulphide concentrate	Pt, Pd, Rh, Au, Ag
PTM-1	, sulphide matte	Pt, Pd, Rh, Au, Ag
PTA-1	, platinum sand	Pt



example, the next slide shows the very obvious trend in the sales of gold ore MA-1, and I believe, the reason is known to all of us here. The sales of gold ore MA-2 which has a gold concentration about one tenth of that of MA-1 has also been very popular since its release last year.

CCRMP offers a suite of four soil RMs. There is a fifth soil sample available internationally from IAEA which is certified for more elements. However CCRMP soils offer a better chance of matching the matrix of samples. Indeed, this is one consideration that can never be overlooked in the use of RMs. To be most effective, RMs should resemble the samples as closely as possible in overall composition. Analysts are only too well aware of the matrix effect. This variety in the type of ores, precious metal materials and soils

SOILS

RM		Certified Constituent
		Ag, Ca, Fe, K, Mg, Mn, Na, P, Si, Ti, Cr, Cu, Hg, Ni, Pb, Sr, V, Zn
SO-1	, clay	except Na, Sr
SO-2	, ferric-humic podzol	except Na, P, Ni
SO-3	, calcareous till	except Ca, Mg, Ti, V
SO-4	, black chernozemic	except Na, Si, Hg

is one aspect that CCRMP has striven for in its preparation of RMs.

The next slide lists the uranium RMs available from CCRMP. The aim was to provide RMs from the major uranium mining ores of Canada, e.g., Elliot Lake, Ontario and Beaverlodge, Saskatchewan. With the closing down of the latter, CCRMP will in future add at least one sample from the Rabbit Lake-Key Lake area of Saskatchewan.

In the past year, CCRMP undertook successfully an interlaboratory program to certify four of its uranium ores, DL-1a, DH-1a, BL-4a, AND BL-5, for radium-226 activity. These are now available for this purpose. A similar endeavor is underway currently for lead-210 activity and it is hoped that these RMs can be certified for both radionuclides next year.

Also in this past year, CCRMP was asked by the National Uranium Tailings Research Program to

URANIUM ORES

RM		Certified Constituent	Radionuclide
DL-1a	, ore, waste rock	U, Th	Ra-226
DH-1a	, ore	U, Th	Ra-226
BL-1	, ore	U	
BL-2	, ore	U	
BL-2a	, ore	U	
BL-3	, ore	U	
BL-4	, ore	U	
Bl-4a	, ore	U	Ra-226
BL-5	, low-grade concentrate	U	Ra-226

			Provisional values for
UTS-1	, tailings	Fe, Ti, Al, Ca, Ba, U, Fe, Ti, Al, CA, Ba, U, Th, S(total), Sulphate, as above plus Ni, As	Ra-226 Ra-228 Th-228 Th-232 Pb-210
UTS-2	, tailings		
UTS-3	, tailings		
UTS-4	, tailings		

prepare four uranium tailings samples for use as compositional RMs. Recommended values for 9 to 11 elements or constituents as well as provisional values for 5 radionuclides were assigned.

The other remaining RMs of CCRMP are shown in the next slide. The copper alloy rods, phosphor bronze discs and the rocks are those RMs I referred to in the history of CCRMP. The niobium and tantalum ores are, I believe, the only such offered for sale today. The interlaboratory programs for their certification was comprised essentially of international laboratories.

The production of RMs is worthwhile in itself. However, the large amount of information on analytical methods derived from the numerous certification programs has a value to the analytical community comparable to that of RMs themselves. For example, where a particular element in a RM was determined by several different methods, unsuspected or subtle biases between methods have been revealed. Such biases affect the economic value (grade, level of impurities, etc.) of ores or concentrates, and in settling disputes in umpire analyses. Also, the availability of a broad range of RMs has allowed the assessment of the performance of an analytical method for the determination of an element at various levels of concentration or in different types of material.

Can RMs actually improve the quality of analytical data? The answer is yes. The next slide shows the results of the round-robin programs for nickel-copper-cobalt ore, SU-1, certified in 1973 and the ore, SU-1a, certified in 1980 to replenish the stock. The lower value for

CERTIFICATION DATA FOR SU-1a AND SU-1

Element	RM	Certified Value (%)	σ_W	σ_B
Ni	SU-1a*	1.233	0.00767	0.0161
	SU-1	1.51	0.0187	0.0279
Cu	SU-1a	0.967	0.00733	0.0115
	SU-1	0.868	0.00928	0.0185
Co	SU-1a	0.041	0.000962	0.00200
	SU-1	0.063	0.00151	0.00464

*Certified in 1980
Certified in 1973

the within- and the between-laboratory standard deviations for SU-1a illustrates clearly that the analytical laboratories involved have improved both their precision and agreement with one another. The same improvement was also observed in the round-robin results for base-metal ore, MP-1, certified in 1972 and for its replacement, MP-1a, certified in 1982.

CCRMP is a centre of expertise and facilities for the preparation of RMs that is unique in Canada. To date, CCRMP has prepared or has aided in the preparation of 8 lake sediments for the Canada Centre for Inland Waters, 2 marine sediments for the National Research Council of Canada and several river and lake sediments for the Geological Survey of Canada. In addition, I should like to mention that the preparation of the reference soils was a cooperative venture between CCRMP and Agriculture Canada. The preparation of the non-ferrous dust, PD-1, was in conjunction with the Air Pollution Technology Centre of Environment Canada.

In summary, I believe that I can safely state that CCRMP plays a significant role in meeting the needs of a multitude of RMs by Canadian laboratories.

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PREPARATION AND USES OF POWDER COMPOSITIONAL REFERENCE MATERIALS: STATISTICAL CONSIDERATIONS

by

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HIGHLIGHT

Methods for preparation of reference materials are described briefly. Various methods of certification are discussed from the statistical point of view; these include certification by consensus, by definitive method and variations thereof. A general method of using these reference materials for checking an analytical method is prescribed. A statistical justification for this prescription is given.

1. INTRODUCTION

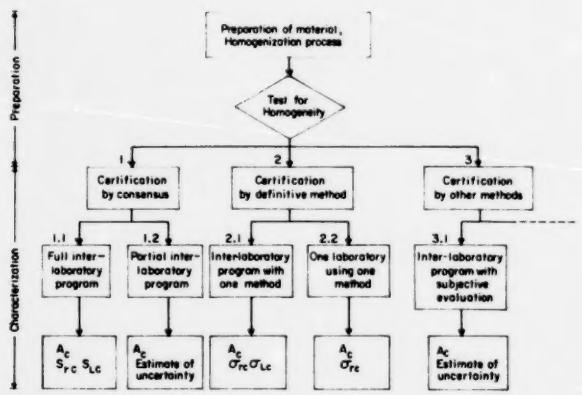
Compositional reference materials (RMs) are generally used either for calibration (reagent or equipment) or for checking an analytical method to see if it has sufficient precision and accuracy. In both cases, the purpose is to determine if the reagent, equipment or method upon application to the RM, can produce results equal to the certificate value. In order to make a proper comparison with the certified value of a RM, the user should know the meaning of this value, which depends on the method of characterization used during the certification of the RM.

2. PREPARATION OF POWDER COMPOSITIONAL RMs

Preparation of a powder compositional RM is illustrated schematically in Figure 1. It consists of two general steps: (1) homogenization and division (bottling) and (2) characterization.

2.1. Homogenization

A bottle of RM that a user has in his laboratory is a sample of a much larger batch that the producer prepared. The composition given in the certificate is the result of analyses obtained from samples taken from the batch. The precision of the certified value, therefore, depends partly on the homogeneity of the batch. This factor contributes directly to the magnitude of sampling errors.



By nature, materials such as ores, rock, etc. are inhomogeneous in the extreme. The question is whether a given material is sufficiently homogeneous for the intended uses of a RM.

Homogeneity of a RM can be partitioned into two parts: the long range or between-bottles homogeneity and the short range or within-bottle homogeneity. For most applications, the between-bottles homogeneity is the more important of the two. Furthermore, it is fixed when the material is bottled and is entirely the responsibility of the producer.

From a statistical point of view, a material is sufficiently homogeneous for use as a RM if the between-bottles component of variation is statistically insignificant with respect to the within-bottle variation which is statistically insignificant with respect to the within-method variation.

In the case of ore RMs, homogeneity is achieved by grinding, usually to minus 200 mesh, and blending the powder. Two opposing factors ensue from this process. Statistically, the finer the material, the smaller the sub-sample size required to achieve the desired precision. However, from a mineralogical point of view, the finer the material, the greater is the chance of segregation occurring between minerals of different density. The balance of these two opposing factors limits the degree of homogeneity of the reference ores.

2.2. Characterization of a RM

Once the material has been homogenized and bottled, it must be then characterized (analysed) to obtain the estimate of the true value of the element content. The strategy chosen for characterization depends on the complexity of the analytical method required and the resources available to the producer. There are various schemes available; each has its own concept. They are:

(a) characterization by consensus

(b) characterization by definitive method

(c) characterization by other methods

Only characterization under categories (a) and (b) will be discussed in this paper.

2.2.1. Characterization of a RM by consensus

The candidate RM is analysed by a number of laboratories, each using methods of their own choice. The consensus value, usually the mean (but it could be some other estimate for central value, i.e., median, mode, etc.), is used for the certificate value.

Two assumptions are made in this scheme:

(1) that there exists a population of laboratories that are equally capable in determining the composition of the RM to provide unbiased results;

(2) that the difference between individual results, both within- and between-laboratories are statistical in nature.

Each result is considered to be an unbiased estimate of the true value of the element content. The mean of all results is therefore assumed to be the best estimate of the true value.

There are two extreme variations within this scheme.

2.2.1.1. Characterization by interlaboratory program

The experimental design of this program is illustrated schematically in Figure 2. Randomly selected sample bottles from the stock are distributed to the participating laboratories. Each is to perform a predetermined number of replicate determinations for the elements of interest from each bottle of sample. If the results are to be used to confirm the homogeneity of the material, at least two bottles of sample should be analysed by each laboratory; otherwise, one bottle for each laboratory is sufficient. A minimum of 10 laboratories, each performing five replicate determinations, is usually necessary for a successful interlaboratory program. The analytical results submitted by the participating laboratories are statistically evaluated. Figure 3 shows an example of the procedure of this evaluation. The following statistics are usually reported as the results of this evaluation: A_c, $V[A_c]$, S_{rc} and S_{Lc} (see Definition of Symbols for the meaning of these symbols).

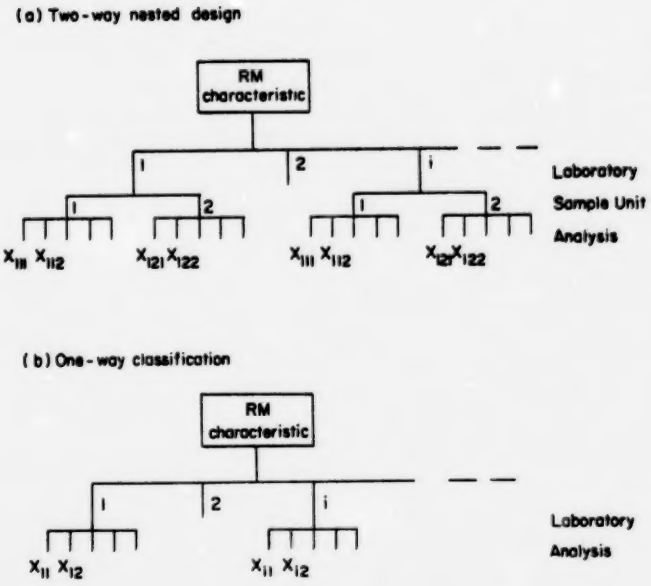


Figure 2. Schematic diagram of experimental design of an interlaboratory program.

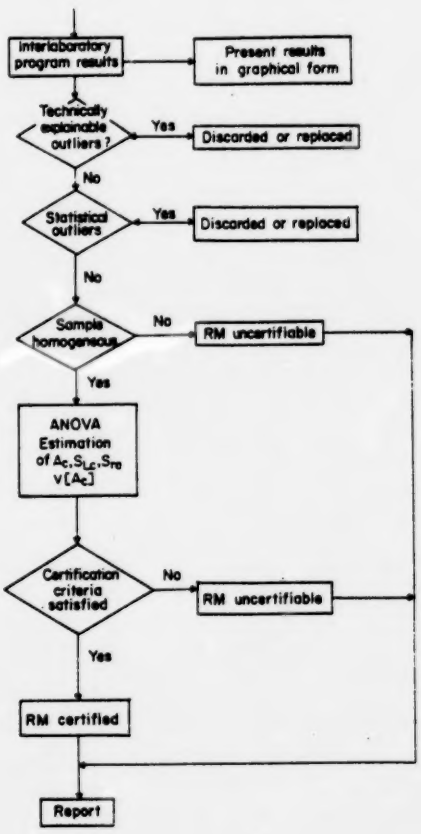


Figure 3. Schematic diagram of statistical evaluation of analytical results for interlaboratory program for characterization of RM.

2.2.1.2. Characterization by partial interlaboratory program

In certain specialized fields, sometimes it is either impossible or impractical to determine the consensus value by a full interlaboratory program. In this case the producers may choose a small number (3 to 5) of "expert" laboratories to analyse the candidate RM. The consensus value A_c is then derived from the agreement between these laboratories. No formal statistical evaluation is performed on the analytical results. The precision of the estimated consensus value is estimated from "chemical" considerations.

2.2.2. Characterization by definitive method

A "definitive method" is an analytical method that is capable of providing the highest accuracy among all methods for determining the value of the element content. Using this scheme for characterization of a RM implies the existance of such method. There are two extreme variations.

2.2.2.1. Interlaboratory program using the definitive method

This scheme is usually chosen when the definitive method is well known such as a standard method. The experimental design is the same as those described in clause 2.2.1.1 except that all participating laboratories use the same method. The statistical evaluation is the same, except that all statistics estimated are referred to those of the definitive method. A_c, $V[A_c]$, σ_{rc}, and σ_{Lc} are usually given in the certificate.

2.2.2.2. One laboratory using the definitive method

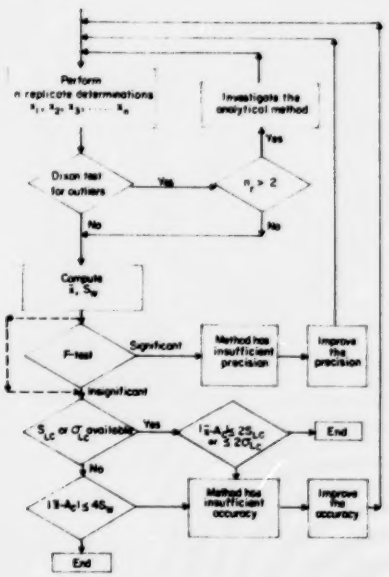
In specialized cases where the definitive method requires a specialized skill or facility, this scheme may be advantageous. This method of characterization is usually performed by either a national or industry reference laboratory. The user of this type of RM should be aware that he or she compares his/her results against those obtained by the "reference" laboratory. The statistics presented in the certificate are A_c, the overall mean and σ_{rc}, the within-laboratory standard deviation of the definitive method as it was performed by an "expert" certifying laboratory.

3. USES OF POWDER COMPOSITIONAL RM

The uses of RMs fall into two categories: (a) for calibration and (b) for checking an analytical method.

For calibration purposes, the user needs only the certificate value. He/she assumes that this value, regardless of how it was derived, is the best estimate of the true value. This value is then transferred directly into the instrument/reagent to be calibrated.

The more prevalent use of a RM is for checking an analytical method to see if it has sufficient precision and accuracy. Because of the inherent error in any analytical method, including those used to characterize RMs, it is highly unlikely that the result produced by the analytical method to be tested will be exactly the same as that of the certificate value. A certain acceptable tolerance limit must be defined for each RM. This limit depends partly on how the RM has been characterized. The following criteria are used to judge an analytical method by applying it to a RM.



(a) Precision

An analytical method is judged to be sufficiently precise if, upon application to a RM, it produces results that are statistically as precise as the precision stated in the certificate value.

(b) Accuracy

An analytical method is considered to be sufficiently accurate if, upon application to a RM, it produces results that do not differ from the certificate value by more than can be accounted for by statistical fluctuation.

3.1. General procedures for checking an analytical method by an RM (Figure 4)

3.1.1 Check of the RM

Before using a RM, the following should be checked:

(a) Certificate - certificate value, precision, method of characterization, suggested sub-sample weight and date of certification (particularly for a relatively unstable RM).

(b) Visual check - segregation, discoloration and quantity.

3.1.2 Analysis

Perform n replicate determinations (from separate sub-samples) using the analytical method that is being examined. It is suggested to use n = 10 for a one-time investigation. For a periodic check of accuracy of an analytical method, n = 2 for each period is sufficient; however the total number of replicates should be greater than 10.

3.1.3 Outliers

Investigate if any of the analytical results is a suspected outlier. Use an outlier test such as the Dixon test (Annex A) for this purpose. If an outlier is found, investigate the physical cause. If more than 20% of the results are found to be outliers and no physical cause can be identified, reinvestigate the analytical procedure.

3.1.4 Mean and standard deviation

Compute the following statistics

$$\bar{X} = \sum_{i=1}^{i=n} X_i/n \quad \text{- mean}$$

$$S_W = \sqrt{\frac{(X_i-\bar{X})^2}{n-1}} \quad \text{- estimated within-laboratory standard deviation}$$

n is the number of analytical results remaining after rejection of outliers.

3.1.5 Precision check

This check can only be performed if the S_{rc}, within-laboratory standard deviation is given in the certificate, otherwise proceed to 3.1.6.

Compute $$F = \frac{S_W^2}{S^2_{rc}}$$

Compare F against $F_o = F_{0.95,n-1,DF_c}$ obtainable from any statistic books or from (1). If the degree of freedom DF_c is not given in the certificate, use $DF_c = 60$.

$F \leq F_o$: the analytical method is sufficiently precise

$F > F_o$: the analytical method is not as precise as those used for characterization of the RM

3.1.6 Accuracy check

(a) If the between-laboratories standard deviation S_{Lc}, or σ_{Lc} is given in the certificate (i.e., RM was characterized by method 2.2.1.1. or 2.2.2.1), then the following test should be used. If

$$|\bar{X} - A_c| \leq 2\, S_{Lc}$$

or

$$|\bar{X} - A_c| \leq 2\, \sigma_{Lc}$$

then the analytical method has sufficient accuracy. Otherwise, it is not considered to be as accurate as the certifying laboratories. Table 1 shows these values ($2\ S_{Lc}$) for reference ores available from the CCRMP (2).

(b) Between-laboratories standard deviation is not given in the certificate; in this case the following test is suggested. If

$$|\bar{X} - A_c| \leq 4\ S_W$$

then the analytical method has sufficient accuracy. In both cases A_c is the certificate value.

Table 1 - Permissible Tolerance ($2\ S_{Lc}$) Values and S_{Lc}/S_{rc} Ratios for Reference Ores Produced by CCRMP

RM	ELEMENT	LEVEL	SIGMAL/SIGMAR	2*SIGMAL
CT-1	TUNGSTEN, WT %	1.0415	1.3	.0662
BH-1	TUNGSTEN, WT %	.4221	1.6	.0285
TLG-1	TUNGSTEN, WT %	.0834	2.0	.0140
BL-1	URANIUM, WT %	.0220	1.2	.0016
BL-2	URANIUM, WT %	.4536	1.1	.0137
BL-3	URANIUM, WT %	1.0215	.9	.0238
BL-4	URANIUM, WT %	.1737	1.2	.0099
BL-5	URANIUM, WT %	7.0910	1.0	.1515
CCU-1	SILVER (UG/G)	139.0395	3.6	15.2928
CCU-1	ALUMINA (WT%)	.2467	1.1	.0217
CCU-1	GOLD (UG/G)	7.5048	1.8	1.0499
CCU-1	COPPER (WT%)	24.7130	1.3	.2309
CCU-1	MERCURY (UG/G)	61.0407	2.0	7.6798
CCU-1	LEAD (WT%)	.1063	2.1	.0236
CCU-1	SILICA (WT%)	2.8093	2.5	.2600
CCU-1	ZINC (WT%)	3.2234	2.6	.1733
CD-1	ANTIMONY, WT %	3.5689	2.3	.1521
CD-1	ARSENIC, WT %	.6629	2.3	.0676
CPB-1	SILVER (UG/G)	625.7892	1.9	26.3855
CPB-1	ALUMINA (WT%)	.2838	1.8	.0391
CPB-1	ARSENIC (WT%)	.0555	1.5	.0136
CPB-1	BISMUTH (WT%)	.0225	2.0	.0040
CPB-1	CADMIUM (WT%)	.0143	1.5	.0016
CPB-1	COPPER (WT%)	.2537	1.8	.0167
CPB-1	IRON (WT%)	8.4285	2.5	.2511
CPB-1	MERCURY (UG/G)	5.4631	1.4	1.5905
CPB-1	LEAD (WT%)	64.7398	2.2	.5857
CPB-1	SULPHUR (WT%)	17.8464	2.2	.4087
CPB-1	ANTIMONY (WT%)	.3561	2.4	.0445
CPB-1	SILICA (WT%)	.7373	1.7	.1087
CPB-1	ZINC (WT%)	4.4174	1.9	.1908
CZN-1	SILVER (UG/G)	92.6369	2.4	10.2317
CZN-1	AL2O3 (WT%)	.2504	2.2	.0433
CZN-1	ARSENIC (WT%)	.0259	2.5	.0089
CZN-1	CADMIUM (WT%)	.1323	1.7	.0085
CZN-1	COPPER (WT%)	.1440	2.2	.0138
CZN-1	IRON (WT%)	10.9346	2.7	.2839
CZN-1	MERCURY (UG/G)	42.9034	2.3	11.9424
CZN-1	MANGANESE (WT%)	.2193	3.0	.0258
CZN-1	LEAD (WT%)	7.4482	1.6	.2457
CZN-1	SULPHUR (WT%)	30.1990	2.8	.7818
CZN-1	ANTIMONY (WT%)	.0524	1.9	.0081
CZN-1	ZINC (WT%)	44.7442	2.2	.5725
DH-1A	URANIUM (WT %)	.2595	.7	.0077
DH-1A	THORIUM (WT %)	.0910	2.7	.0101
DL-1A	URANIUM (WT %)	.0116	1.2	.0013
DL-1A	THORIUM (WT %)	.0076	2.0	.0016
HV-1	COPPER, WT %	.5217	1.1	.0201
HV-1	MOLYBDENUM, WT %	.0575	1.0	.0047
KC-1	LEAD, WT %	6.9790	2.0	.2222
KC-1	COPPER, WT %	.1136	2.1	.0097
KC-1	TIN, WT %	.6676	3.2	.0699
KC-1	SILVER, WT%	.1137	2.2	.0064
KC-1	ZINC, WT %	20.0948	1.3	.2089
MA-1	GOLD, OZ/TON	.5185	.7	.0224
MA-2	GOLD (UG/G)	1.8632	1.6	.2441
MP-1	TIN, WT %	2.4234	1.6	.3129
MP-1	COPPER, WT %	2.1476	2.3	.1131
MP-1	LEAD, WT %	1.9259	1.7	.1054
MP-1	MOLYBDENUM, WT %	.0138	.9	.0028
MP-1	INDIUM, WT %	.0707	1.7	.0067
MP-1	BISMUTH, WT %	.0253	1.8	.0069
MP-1	ARSENIC, WT %	.7910	2.6	.0801
MP-1	SILVER, UG/G	58.4648	3.1	6.7164
MP-1	ZINC, WT %	15.9297	1.4	.2308
MP-1A	ZINC, WT %	19.0159	1.7	.4174
MP-1A	TIN, WT %	1.2844	2.6	.1373
MP-1A	COPPER, WT %	1.4367	1.5	.0365
MP-1A	LEAD, WT %	4.3315	2.8	.1397
MP-1A	MOLYBDENUM, WT %	.0293	3.3	.0044
MP-1A	INDIUM, WT %	.0330	2.2	.0042
MP-1A	BISMUTH, WT %	.0317	3.3	.0062
MP-1A	ARSENIC, WT %	.8376	2.1	.0698
MP-1A	SILVER, UG/G	69.6739	2.5	6.9418
MP-2	SILVER, UG/G	4.9051	2.3	1.0761
MP-2	BISMUTH, WT %	.2457	3.8	.0210
MP-2	MOLYBDENUM, WT %	.2811	3.5	.0386
MP-2	TUNGSTEN, WT %	.6481	3.3	.0695
MW-1	IRON, WT %	66.0816	1.4	.2102
MW-1	FE(II), WT %	1.3564	1.5	.1065
MW-1	AL2O3, WT %	.3023	2.7	.0417
MW-1	SIO2, WT %	4.5856	2.5	.2157
MW-1	CAO, WT %	.0540	1.2	.0085
MW-1	MGO, WT %	.0318	2.2	.0079
MW-1	PHOSPHORUS, WT %	.0112	2.4	.0031
MW-1	POTASSIUM, WT %	.0110	2.3	.0024
OKA-1	NIOBIUM (WT %)	.3714	3.7	.0474
PD-1	LEAD(WT %)	2.6837	3.0	.2872
PD-1	ARSENIC(WT %)	.7662	2.2	.1177
PD-1	MERCURY(UG/G)	388.6250	2.0	66.6286
PR-1	MOLYBDENUM, WT %	.5961	3.1	.0450
PR-1	BISMUTH, WT %	.1115	1.4	.0102
PR-1	IRON, WT %	1.2475	1.9	.0552
PR-1	SULPHUR, WT %	.7934	2.6	.0522
PTA-1	PLATINUM, OZ/TON	.0884	.2	.0065
PTC-1	PALLADIUM, OZ/TON	.3664	.8	.0727
PTC-1	PLATINUM, OZ/TON	.0872	.7	.0194
PTC-1	RHODIUM, OZ/TON	.0177	1.2	.0038
PTC-1	GOLD, OZ/TON	.0188	.8	.0083
PTM-1	GOLD, OZ/TON	.0519	1.0	.0131
PTM-1	PALLADIUM, OZ/TON	.2363	1.1	.0511
PTM-1	PLATINUM, OZ/TON	.1705	.9	.0225
RU-1	ZINC, WT %	2.2372	2.4	.0842
RU-1	COPPER, WT %	.8543	1.8	.0351
RU-1	IRON, WT %	24.4049	2.2	.3223
RU-1	SULPHUR, WT %	21.6161	2.5	.4542
SL-1	SILICA, WT %	35.7342	1.7	.4662
SL-1	LIME, WT %	37.4756	2.5	.7733
SL-1	MAGNESIA, WT %	12.2667	2.4	.6858
SL-1	ALUMINA, WT %	9.6338	1.1	.2661
SL-1	FEO (FE-TOTAL), WT %	.9239	1.5	.1372
SL-1	SULPHUR, WT%	1.2562	2.1	.0936
SU-1	COPPER, WT %	.8677	1.7	.0353
SU-1	NICKEL, WT %	1.5104	1.1	.0526
SU-1A	NICKEL (WT %)	1.2328	1.8	.0327
SU-1A	COPPER (WT %)	.9673	1.3	.0224
SU-1A	COBALT (WT %)	.0407	1.3	.0039
SU-1A	PLATINUM (UG/G)	.4117	1.9	.1480
SU-1A	PALLADIUM (UG/G)	.3703	1.7	.0616
SU-1A	SILVER (UG/G)	4.3483	1.3	.7616
TAN-1	TANTALUM	.2363	1.1	.0217
UM-1	COPPER, WT %	.4317	1.7	.0214
UM-1	NICKEL, WT %	.8801	1.5	.0380
UM-1	COBALT, WT %	.0345	1.9	.0039
SCH-1	IRON, WT %	60.7320	2.2	.3956
SCH-1	SILICON, WT %	3.7788	2.0	.1731
SCH-1	ALUMINUM, WT %	.5087	1.6	.0390
SCH-1	CALCIUM, WT %	.0295	2.9	.0097
SCH-1	MAGNESIUM, WT %	.0201	1.9	.0053
SCH-1	MANGANESE, WT %	.7774	1.9	.0377
SCH-1	TITANIUM, WT %	.0307	1.7	.0072
SCH-1	SULPHUR, WT %	.0074	2.0	.0026
SCH-1	PHOSPHORUS, WT %	.0543	1.2	.0102
SCH-1	MOISTURE, WT%	.2670	3.2	.1667
SCH-1	SODIUM, WT %	.0186	2.6	.0090
SCH-1	POTASSIUM, WT %	.0256	2.6	.0096

*Level = A_c

SIGMA L = S_{Lc}

SIGMA R = S_{rc}

2 S_{Lc} = Permissible tolerance

3.2 Statistical justification

3.2.1. Assumptions

(a) The certificate values are assumed to be the best estimates of the true values of the element contents of the RM.

(b) All errors both within- and between-laboratories are assumed to follow the normal frequency distribution.

3.2.2. Significance level

Significance level $\alpha = 0.05$ is used for all statistical tests.

3.2.3. Number of replicate determinations, n

The number of replicate determinations to be performed directly affects the precision of the estimate of the within-laboratory precision, S_W. Table 2 shows the relation between n and the maximum ratio of the within-laboratory standard deviation of the analytical method and the certification within-laboratories standard deviation, S_W/S_{rc}, at various values of β at $\alpha = 0.05$. β is the probability of accepting the analytical method if the standard deviation is greater than the product of the ratio and the certification value. For example, for n = 10, and the analytical method has passed the appropriate F-test, there is no more than a 5% chance that it has a standard deviation in excess of 2.2 S_{rc}. It is on this basis that n = 10 was recommended in Section 3.1.2.

3.2.4. Accuracy

The accuracy of the analytical method is checked by comparing the mean $\overline{X}$ with the certificate value, A_c.

In addition to the assumptions listed in 3.2.1., it is further assumed that the analytical method is sufficiently accurate if it produces results that would have been used to derive the certificate value had it been used by one of the participating laboratories during the characterization of the RM.

Table 2

Number of replicate determinations, n, required for the comparison of the standard deviation of the analytical method with the standard value.

n	$\sigma = 0.05$			
	$\beta = 0.01$	$\beta = 0.05$	$\beta = 0.1$	$\beta = 0.5$
1	159.5	31.3	15.6	2.73
2	17.3	7.64	5.33	2.08
3	6.25	4.71	3.66	1.82
4	5.65	3.65	2.99	1.68
5	4.47	3.11	2.62	1.59
6	3.80	2.77	2.39	1.53
7	3.37	2.55	2.23	1.49
8	3.07	2.38	2.11	1.45
9	2.85	2.26	2.01	1.42
10	2.67	2.15	1.94	1.40
12	2.43	2.01	1.83	1.36
15	2.19	1.85	1.71	1.32
20	1.95	1.70	1.59	1.27
24	1.83	1.62	1.52	1.25
30	1.71	1.54	1.46	1.22
40	1.59	1.45	1.38	1.19
60	1.45	1.35	1.30	1.15
120	1.30	1.24	1.21	1.11

3.2.4.1 RM characterized by interlaboratory program

There are two contributions to the uncertainty to be taken into account: (1) the uncertainty of the certified value and (2) the uncertainty of the analytical method. The following formula can be used as the criterion for acceptance.

$$|\overline{X} - A_c| \leq 2\sqrt{C + D} \qquad \text{(Eq. 1)}$$

where:

C = uncertainty associated with the certified value;

D = uncertainty associated with the analytical method being examined.

The value of C depends on the method of characterization of the RM.

(a) Characterization by interlaboratory program with multiple methods

$$C = (S_{Lc}^2 + S_{rc}^2/n_c)/N_c \qquad \text{(Eq. 2)}$$

(b) Characterization by interlaboratory program using one definitive method

$$C = (\sigma_{Lc}^2 + \sigma_{rc}^2/n_c)/N_c \qquad \text{(Eq. 3)}$$

For most characterization of RMs by interlaboratory programs such as those conducted by the CCRMP, N_c is usually greater than 10. Consequently C is small in relation to D and can be considered as negligible. The following two categories can then be considered:

(1) RM is used to test a new method (both σ_L and σ_r are unknown).

To be acceptable from the accuracy point of view, this new method must have σ_L equal to or better than the laboratories that participated in the characterization of the RM. In this case

$$D = \sigma_{Lc}^2 + S_{W/n}^2 \quad \text{or} \quad D = S_{Lc}^2 + S_{W/n}^2$$

depending on the type of RM used. For n = 10, $S_{W/n}^2$ becomes negligible and Eq. 1 becomes:

$$|\bar{X} - A_c| \leq 2\, S_{Lc} \qquad \text{(Eq. 4a)}$$

or

$$|\bar{X} - A_c| \leq 2\, \sigma_{Lc} \qquad \text{(Eq. 4b)}$$

(2) RM is used to check a method where σ_L and σ_r are known (such as standard method). In this case:

$$D = \sigma_L^2 + \sigma_{r/n}^2$$

Eq. 1 becomes

$$|X - A_c| \leq 2\sqrt{\sigma_L^2 + \sigma_{r/n}^2} \qquad \text{(Eq. 5)}$$

3.2.4.2. RM characterized by partial interlaboratory program

RMs characterized by this method would not have an estimate of between-laboratories standard deviation, S_{Lc}. Experience within the International Standards work on iron ore analysis shows that an analytical method is generally considered to be well standardized if the ratio of $\sigma_L/\sigma_r = 2$. Based on this experience, it is reasonable to substitute S_{Lc} by $2S_W$ and Eq. 4a becomes

$$|\bar{X} - A_c| \leq 4\, S_W \qquad \text{(Eq. 6)}$$

3.2.4.3. RM characterized by definitive method

Using this type of RM implies comparison of the method and/or reagents/equipment with the definitive method.

3.2.4.3.1. RM characterized by interlaboratory analysis using definitive method

All formulas in clause 3.2.4.1. may be used. Both σ_{rc} and σ_{Lc} refer to the definitive method.

3.2.4.3.2. RM characterized by a single laboratory using definitive method

In addition to the recognition that the definitive method is the best method available, the user concludes that the producer laboratory is capable of applying the method without bias i.e., $\sigma_{Lc} = 0$. This is a very strong assumption and is usually found in the following situation:

(a) when the producer laboratory is a national or industrial reference laboratory where "superior" resources are available

(b) when the analysis involves a certain "art" and specialized skill is required.

If the above assumption is satisfied Eq. 6 may be used as criterion for acceptance.

Definition of symbols

A_c = certified value of an element content. A_c is usually derived from the overall means of the results of certification program (or mean of the laboratory means) or in some cases other central values such as the geometric mean, the median, etc.

$V[A_c]$ = variance of A_c, a measure of precision of the consensus value. Alternatively, the precision may be expressed in terms of a confidence interval (usually 95%). This means that if the interlaboratory program is repeated one hundred times, and each time a confidence interval is constructed, 95% of these interval will include the true A_c.

S_{Lc} = between-laboratories standard deviation derived from the results of an interlaboratory program for certification of a RM where each participating laboratory uses an analytical method of its own choice.

S_{rc} = within-laboratories standard deviation derived from the results of an interlaboratory program for certification of a RM where each participating laboratory uses an analytical method of its own choice.

σ_{Lc} = between-laboratories standard deviation derived from the results of an interlaboratory program for certification of a RM where all of the participating laboratories use the same analytical method.

σ_{rc} = within-laboratories standard deviation derived from the results of an interlaboratory program for certification of a RM where all of the participating laboratories use the same analytical method.

σ_L = between-laboratories standard deviation of an analytical method derived from the results of an interlaboratory program for the precision experiment of the analytical method.

σ_r = within-laboratories standard deviation of an analytical method derived from the results of an interlaboratory program for the precision experiment of the analytical method.

S_W = within-laboratory standard deviation of the analytical method to be tested, derived from the analytical results of the test.

N_c = number of laboratories (excluding outliers) that participated in the certification of the RM.

n_c = average number of replicate determinations performed by each participating laboratory for the certification program.

n = number of replicate determinations performed during the testing of the analytical method.

X_i = individual result produced by the analytical method to be tested.

n_r = number of suspected outliers among the results of testing the analytical method.

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2. Description of the material, methods of preparation and characterization of RMs produced by CCRMP can be found in the following reports.

RM	REPORT NO.
Antimony Ore CD-1	CM 77-62
Blast Furnace Slag SL-1	CM 77-57
Copper Concentrate CCU-1	CM 79-16
Copper-Molybdenum Ore HV-1	Mines Branch TB 167
Gold Ore MA-1	MRP/MSL 75-29 (TR)
Gold Ore MA-2	CM 81-13E
Iron Ore SCH-1	MRP/MSL 75-168 (TR)
Iron Ore MW-1	CM 82-16E
Lead Concentrate CPB-1	CM 79-15
Molybdenum Ore PR-1	Mines Branch TB 139
Nickel-Copper Ore SU-1A	CM 80-9
Nickel-Copper Ore UM-1	Mines Branch TB 177
Niobium Ore OKA-1	CM 81-1E
Noble Metals-Bearing Sulphide Concentrate PTC-1	Mines Branch TB 176
Noble Metals-Bearing Nickel-Copper Matte PTM-1	Mines Branch TB 138
Non-Ferrous Dust PD-1	CM 81-7E
Tungsten Ore BH-1 and TLG-1	CT-1, CM 76-5
Uranium-Thorium Ore DL-1a	CM 80-10
Uranium-Thorium Ore DH-1a	CM 80-11E
Uranium Ores BL-2, BL-3 and BL-4	BL-1, CM 77-64
Uranium Ores and BL-4a	BL-2a, CM 82-6E
Uranium Ore BL-5	CM 79-4
Zinc Concentrate CZN-1	CM 79-14
Zinc-Lead-Tin-Silver Ore KC-1	CM 78-2
Zinc-Tin-Copper-Lead Ore MP-1a	CM 82-12E

These reports can be obtained from CANMET, Energy, Mines and Resources Canada, 555 Booth Street, Ottawa, Canada, K1A 0G1.

3. "Handbook of tables for probability and statistics"; 2nd ed., The Chemical Rubber Co., Cleveland, OH 44128; 1968.

EVALUATION AND APPLICATION OF SPECIAL TYPES OF REFERENCE MATERIALS

by

S. Abbey

HIGHLIGHT

The special nature of reference materials for use in geological studies is described in relation to the number of constituents of interest and of the laboratories participating in the characterization. The occurrence of skewed and incoherent data and their resolution into a meaningful, acceptable distribution is discussed. In this context, the Geological Survey of Canada "select laboratories method" and the Dybczynski scheme for data resolution are compared.

Finally, a procedure for the use of this type of reference material is suggested.

EVALUATION AND APPLICATION OF SPECIAL TYPES OF REFERENCE MATERIALS

by

Sydney Abbey (retired)

Geological Survey of Canada

The purpose of this talk is to acquaint you with some of the special problems that may arise in the evaluation and application of some reference materials that do not readily lend themselves to treatment by the techniques outlined by the preceding speakers. I shall be concentrating mainly on silicate rocks and minerals because they represent most of my experience in this field. Some of the ideas expressed may also apply to other materials, notably soils and sediments.

How does a rock differ from an ore? After all, an ore can be regarded as a rock which happens to contain an economically significant concentration of an industrially useful constituent. The real difference lies in the analytical treatment. An ore is normally analysed for the constituent that makes it an ore - a gold ore for gold, a nickel ore for nickel, etc. Frequently, an ore must be analysed also for potential byproducts and for undesirable impurities which may cause problems in processing or in the final product. Analysts involved in ore analysis - particularly if the samples are intended for use as reference materials - generally are skilled in the analysis of the type of material of interest.

Rock analyses, on the other hand, are normally performed in support of geological studies. Reference samples for rock analysis are intended for use in the analysis of all silicates, and may also be useful in geochemical work. The most significant characteristics of a rock analysis are that it requires the determination of nearly all constituents of the sample - major, minor and trace - and that the concentrations of all constituents can vary over a wide range. Needless to say, true "complete" analysis is never really attained. It follows, then, that a rock reference sample must be evaluated for its content of as many of the elements in the Periodic Table as possible, as well as for the different states of a few key constituents - e.g. ferrous and ferric iron, carbonate and non-carbonate carbon, H_2O^- and H_2O^+. For those unfamiliar with the last two terms, H_2O^- refers to the superficial water that can be removed by mere drying at 105-110°C, H_2O^+ to the water content requiring heating at much higher temperatures, generally in the presence of a flux.

So, the first problem in evaluating a suite of rock reference samples is: "Who will do the analysis?". The first slide shows a breakdown of the laboratories that contributed data on three Canadian rock reference samples, in an operation begun about 10 years ago. You will observe that government laboratories were the source of much of the analytical data. Those classified as "geological, etc." included some whose main interests were in the environment and in marine and inland waters. Not surprisingly, the more geologically-oriented laboratories tended to

NUMBER OF CONTRIBUTING LABORATORIES

(Samples SY-2, SY-3, MRG-1)

TOTAL	76
GOVERNMENT	38
Geological, etc.	27
Nuclear	5
Other	6
ACADEMIC	34
INDUSTRIAL	4

report the more consistent results, although there were some exceptions. The nuclear laboratories did best with the more difficult trace elements, but some of their results for elements at higher concentrations were disappointing.

Geology and chemistry departments in universities were another major source of data, but their results were, in general, less satisfactory. Very few of such departments have staff members whose major activity is the performance of actual analyses. In many cases, analytical work is done as a sideline by workers whose prime interest is in applying the results, not in obtaining them.

The laboratories referred to in this slide were initially selected on the basis of the quality of their work in earlier programs; others were included because of their ability to determine difficult trace elements. The next slide indicates how far afield one has to go to find such laboratories.

With participating analysts scattered all over the world, the mere logistics of the operation can become quite a headache. Deadlines for reporting results are difficult or impossible to meet. The collaborative analytical program on these particular samples was begun in 1973: a preliminary report appeared in 1975; a supplement in 1976; a more-or-less final report only in 1979. The term "more-or-less final" is used because considerable additional data have appeared in the literature since 1979. It may be possible to prepare an update, in which a few additional usable values could be derived and some tentative assigned values might be upgraded.

With results on hand from 76 different laboratories, surely it should be possible to arrive at reliable concentration values for many constituents. In fact, things are not necessarily so straightforward. The next slide illustrates how "imbalanced" the results from 76 sources can be. At first glance, derivation of usable values for silica, carbon dioxide and nickel would appear to be feasible. Silver, palladium and selenium are another matter. Although there are somewhat more results for silver than for the two other cited trace elements, they are not in good accord with one another.

NUMBERS OF RESULTS REPORTED

(Selected constituents)

CONSTITUENT	SY-2	SY-3	MRG-1
SiO_2	63	64	57
CO_2	28	27	29
Ag	6	7	7
Ni	28	31	38
Pd	2	0	0
Se	2	3	3

But even for nickel, where we have a reasonable quantity of data for all three samples, things look less hopeful when we look at the distribution of results in one of the samples, on the next slide. The histogram shows a severely skewed distribution. The value 125, which should really be shown off scale, is an obvious outlier that should be rejected before any attempt at an estimate of the true nickel content. Are there

GEOGRAPHIC DISTRIBUTION OF LABORATORIES

EUROPE	30
NORTH AMERICA	29
ASIA	7
AFRICA	5
AUSTRALASIA	5
TOTAL	76

NICKEL (ppm) IN SY-3 - DISTRIBUTION OF RESULTS

("Numerical histogram")

```
9
9
8.5
8
8
8     14
8     14
7.4   14
7     13.7
7     12
7     12      18
6.9   11      17
6.5   11      17
5.2   10.     16.     .     24.     28.     34.     .........125
```

any others that should be eliminated? In any case, would the arithmetic mean of so lopsided a distribution be a reasonable estimate of the truth?

The figures shown in the last two slides were taken from a large mass of data, but they are typical of the conditions encountered in collaborative analysis of proposed reference samples of rocks. With such messy data, it is not easy to arrive at good usable values. Many computational schemes have been proposed, using medians, means (with and without rejection of outliers), modes, etc. When some of those schemes were applied to the data for nickel in SY-3, resulting so-called "best values" ranged all the way from 7.4 to 16.0 ppm.

DERIVED VALUES FOR NICKEL IN SY-3 (ppm)

Mean (all data)	16.0
(outliers removed, various schemes)	12.4
	10.4
Geometric Mean	11.9
Median (all data)	11.0
(outliers removed, various schemes)	10.5
	9.5
Modes (various schemes)	10.4
	8.8
	8.0
	7.9
	7.4

The schemes proposed thus far may be roughly divided into two categories: (a) those that depend entirely on mathematical treatment, and (b) those based on purely subjective considerations. Some, of course, embody aspects of both approaches. Generally, those workers who have been most deeply involved in the preparation and evaluation of rock reference materials have tended to favor the pragmatic side. (Slide 7).

The French group, operating out of the Centre de Recherches Pétrographiques et Géochimiques, in Nancy, originally favored the "preferred mean" (9) --i.e., the mean of remaining values for each major and minor constituent after rejection of values removed from the overall mean by more than one standard deviation. A purely subjective estimate, generally close to the median, was used for trace elements. Later, however, they computed various central measures (means, medians, modes, etc.) and then used a knowledgeable subjective choice from them as recommended value (10).

The South African program, operated by the then National Institute for Metallurgy, used a scheme much like the later French one (11).

The American approach, as used by the U.S. Geological Survey (12), has never been described in the literature, but appears to be based on the means of remaining values after rejection of outliers, but with a measure of subjective judgment in favor of results for some trace elements reported by certain favored analytical techniques.

A highly pragmatic system developed at the Geological Survey of Canada was described in detail in a recent report (1), which also described other proposed evaluation systems and comparisons between them. The GSC scheme, known as the "select laboratories method", assumes that erratic distributions of data are not due to random inaccuracies, but to systematic error. The system involves assigning a "rating" to each participating laboratory, based on where its results fall within the various distributions, and using only the results from the better laboratories to arrive at a "best value".

Not only is there no generally accepted method for resolving incoherent data, there are not even accepted criteria for assessing the validity of values derived by the various schemes. Those who have proposed such schemes have generally been satisfied with showing that their results came "close" to those found by others. The range of derived values for nickel in SY-3 shows how "unclose" they can be.

Two "tests of validity" have been proposed in work emanating from the GSC: the summation and the "iron-oxide compatibility".

Because a rock analysis is supposedly "complete", the sum of all the constituents should come close to 100%. Even that self-evident truth has some strings attached to it: since most major and minor constituents are reported as oxides, trace elements must be added in as oxides; an oxygen correction must be applied in proportion

to the contents of sulphide sulphur and of any halogens present; compensatingerrors can confuse the issue - to name but a few of those "strings".

So-called "complete" analyses of rocks, if done at least in part by purely chemical methods, can yield values for ferrous and total iron, ferric then being determined by difference. Instrumental analyses generally report only total iron. In resolving data from a large number of analyses, if the three forms of iron are treated as three separate consitutents, total iron can be calculated from the derived values for ferrous and ferric. Total iron can also be derived from reported values for total iron as such. If the two resulting values for total iron are reasonably close together, some confidence in the derivation scheme is possible. "Reasonably close together" is not a very precise concept, but the principle involved can be used in comparing the validities of two or more evaluation schemes. Like the summation test, the iron-oxide compatibility also has its pitfalls, the ferrous determination being the most error-prone of all methods for major rock constituents.

In the recent report mentioned a moment ago (1), and in two earlier papers (2,3), the foregoing tests were used to support the claim of superiority for the select laboratories method.

Another recent report (4) gives information and analytical data on four reference samples of Canadian iron-formation rocks, FeR-1, -2, -3, and -4. Among other things, those samples emphasize the difference between an ore and a rock. Where an iron-ore reference sample would normally be evaluated for about a dozen major and minor constituents, each of the FeR samples was evaluated for 16 major and minor constituents and for 17 to 29 trace elements, numbers which may well be further increased as more analytical data become available. Ironically enough (no pun intended), all four FeR samples could qualify as iron ores, but they were under study as rocks.

Among the other approaches to the resolution of incoherent analytical data in inter-laboratory programs on rock reference samples, many have been based on the assumption that elimination of a sufficient number of outliers will leave a distribution sufficiently close to "normal" to make the arithmetic mean the best approximation of the true concentration of a particular constituent. One of the most rationally derived of such schemes is that of Dybczynski (5), who used four different statistical tests to eliminate outlying values, and then accepted the mean of the remaining values as best approximation of the truth. Further, Dybczynski applied his scheme to collaborative analytical data on a group of water samples of accurately known trace-element contents. Results served to support the validity of his computation scheme. Dybczynski then applied the same scheme to analytical data collected on two solid samples, a soil (6) and a lake sediment (7), a step I personally consider questionable. There is a very great difference between trace elements in a homogeneous aqueous solution on the one hand, and major, minor and trace constituents in a heterogeneous solid like a rock, soil or lake sediment, on the other.

A former colleague at GSC, a physicist who believes that any scientific problem should be treated without resort to subjective considerations, calculated "best values" for a large number of constituents of the FeR samples by means of the Dybczynski method, using the same raw data as had been used in the evaluation by the select laboratories method. Many of the results produced by the two methods were identical or very close to one another, but there were a few conspicuous exceptions. It was therefore decided to apply the "tests of validity" to both sets of results.

First, the two tests mentioned earlier were used, namely the summation and the iron-oxide compatibility. A third test was also applied: the "analytical linearity", based on the following exerpt from a paper presented at an international meeting in 1976 (8):

> "... given a set of, say, at least four reference samples, the assigned concentration values for a particular element in the different samples can be compared to one another by taking all of the samples through a reliable analytical method and plotting the

COMPARISON TESTS ON FeR DATA

(Select laboratories vs Dybczynski Method)

TEST	SL BETTER	DM BETTER
(a) Summation	3	1
(b) Iron Oxides compatibility	4	0
Least squares straight lines:		
(c) Slope closer to unity	10	7
(d) Intercept closer to zero	10	7

final signal (weight, titration, absorbance, etc.) against the assigned concentration values. If the plotted points are sufficiently close to a straight line, the correctness of the assigned values for the same element in the different samples would be confirmed, at least relative to one another. All may still be subject to a consistent bias..."

For the problem at hand, that test was modified by first selecting those constituents showing the greatest differences between the values derived by the two methods. For each constituent, a laboratory was selected such that its reported value lay closest to the means of those derived by the SL and DM methods. That laboratory's results were then plotted as ordinates against the SL values as abscissae, and the equation for the least-squares straight line through the four points (representing the four samples) computed. A similar straight line equation was computed for a plot of the same laboratory's results against the DM values. Ideally, such plots should produce straight lines with a slope of unity and an intercept of zero.

In this slide, we have the scores on the three tests: (a) which method gave summations closer to 100% on each of the four samples, (b) which method gave better iron-oxide compatibility on each of the four samples, (c) which method produced a straight line with a slope closer to unity on each of 17 constituents, and (d) which method produced a straight line with an intercept closer to zero on each of the same 17.

One more test was also used, this time to determine the effect of removing the "Dybczynski outliers" on the skewness of a distribution. If the mean of the remaining values is to be a fair measure of the truth, one might expect the removal of outliers to reduce skewness to insignificance. Using reported values for six constituents of all four samples, the skewness of each distribution was computed before and after removal of the outliers detected by the Dybczynski scheme. Results are shown in the next slide. As you can see, in only one case in 24, the removal of outliers effectively eliminated skewness; in two other cases, removal of outliers actually increased skewness; most of the cases where no outliers were detected involved relatively low skewness in the initial distribution; others showed skewness greater than some in which actual outliers were found. It follows that if there is measurable residual skewness in the trimmed distributions, the arithmetic mean cannot be expected to be a reliable measure of the true concentration.

All of the foregoing is intended to show how the evaluation of reference samples of rocks can lead to real problems - over and above those encountered with ore samples. One must not forget, however, that none of the validity tests cited are fool proof. They may lend support to our hypotheses, but not confirmation.

In preparing reference samples of silicate rocks, the crushing, grinding and homogenisation steps are much the same as with ore materials. However, because of the great and varied range of possible compositions in rocks, a large number of reference samples are needed. Also, the almost unquantifiable uncertainties in the raw data make it practically impossible for the derived concentration values to attain the degree of confidence that is possible with ore samples.

The "uncertain uncertainties" in the assigned values for the concentrations of constituents of rocks reference samples must be borne in mind in the use of such samples. It would be unwise, for

CHANGE IN SKEWNESS ON REMOVING OUTLIERS

TOTAL NUMBER OF DISTRIBUTIONS TESTED	24
SKEWNESS ELIMINATED	1
SKEWNESS REDUCED BUT NOT ELIMINATED	13
SKEWNESS UNCHANGED (NO OUTLIERS)	8
SKEWNESS INCREASED	2

example, to depend on a single reference sample in checking out a new method, in running controls in everyday analysis, in comparing results between laboratories, etc. In using a suite of, say, at least four reference samples, the uncertainties in the assigned values would tend to "balance out", particularly in calibrations. There is another advantage in such practice, and that is that the concentrations of all other constituents of the reference samples in the suite are varying in a nearly random manner as the desired element varies over the desired concentration range. If the resulting calibration points fall acceptably close to a straight line or other appropriate smooth curve, we have, as mentioned earlier, supporting evidence of the validity of the assigned concentration values for the desired element in the reference samples. We also have evidence that no interferences are present. Simply put, a calibration based on a sufficient number of suitable reference samples can be much more informative than one based on standard solutions or on weighed portions of pure solid compounds of the desired element.

In closing, let me emphasize that the foregoing should not be regarded as a rejection of rigorous statistical methods, but merely to point out that the "fuzzy" nature of the analytical data on rock reference samples does not justify the use of rigorous statistical treatment.

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INTERNATIONAL STATUS OF REFERENCE MATERIALS

by

Henry F. Steger

HIGHLIGHT

The current international status of reference materials, RMs, is reviewed. The number and varying nature of RMs as well as the number of producers is touched upon. Some examples are given of the cooperation in the preparation of RMs by producers from different nations in order to avoid duplication of effort. Finally, the goals and achievements of REMCO, the Council Committee on RMs of ISO, are discussed with respect to their implication for users and producers alike.

INTERNATIONAL STATUS OF REFERENCE MATERIALS

by

H.F. Steger

The purpose of this presentation is to discuss the current international status of RMs. By this I do not intend to present an extensive listing of the various RMs available world-wide. I could do this most effectively by providing each of you with a catalogue of RMs from all producers. Rather I will try to describe how to get the information on what and from whom currently available RMs may be obtained. I also want to mention examples of cooperation in the preparation of RMs between producers from different countries and finally I will describe the goals and achievements of REMCO, the Council Committee on Reference Materials of the International Organization for Standardization, ISO.

I mentioned in the first presentation that no one producer of RMs could meet the world's requirements for the many types of RMs and that as a consequence most industrialized nations have programs to produce RMs essentially for national purposes. It has been estimated that over 1000 new RMs will be needed in the next decade. It is little wonder therefore that there are at least 130 producers of RMs of all types in the western world alone. If only compositional RMs such as ores, rocks and metal alloys are considered, there are at least 39 producers therein. The slide shows a breakdown by country and nature of the producer.

RM PRODUCERS

Country	Number	Industrial	Government
France	9	6	3
Japan	8	7	1
USA	5	4	1
UK	5	5	-
Sweden	2	2	-
Spain	2	-	2
Canada	2	-	2
West Germany	1	-	1
Brazil	1	-	1
South Africa	1	-	1
*International	3	BCR, IAEA, WHO	

Classifying RMs producers as government is straight forward. These are agencies within a government framework that have been given the mandate to or have assumed the responsibility to prepare RMs to satisfy the national need. All other producers have been classified as industrial; these include profit-making agencies such as Bureau of Analysed Samples of the United Kingdom or individual companies or the federated society of several companies which prepare RMs for self interest. Examples are British Aluminium Company and Iron and Steel Institute of Japan, respectively. Altogether, the 39 producers referred to in the slide represent approximately 250 reference ores, concentrates, rocks soils and cements, over 1140 non-ferrous metals and alloys and over 1250 iron and ferrous alloys in various sample forms. With such numbers of RMs available, a directory of RM and source is necessary.

The two producers of RMs in Canada are CCRMP of course and the National Research Council which offers two marine sediments certified for 25 constituents as well as a reference sea water sample. The Canada Centre for Inland Waters and the Air Pollution Technology Centre, both of Environment Canada, have prepared several river and lake sediments and a non-ferrous dust from INCO, respectively, for use as RMs in analytical data quality assurance programs rather than for sale. Samples may however sometimes be obtained free of charge if used for the intended purpose or in return for analytical results. The Geological Survey of Canada has also prepared several river and lake sediments for use as RMs in geochemical analysis but it is expected that these will be made available through CCRMP.

Of the international producers of RMs, BCR, le Bureau Communauté de Référence, is a multi-national organization of the European

Economic Community. Its goal with regard to RMs is to complement the production of national producers. Its multi-national character is advantageous in giving access to a much wider selection of participating laboratories. IAEA, the International Atomic Energy Agency, and WHO, the World Health Organization, are as might be expected concerned primarily with RMs in the nuclear and health realms, respectively.

The production of a RM is time-consuming and expensive process and it is important therefore that duplication be avoided wherever possible. For this reason, cooperation in the production of RMs between agencies from different countries is occurring more and more frequently. I will illustrate only two examples of such joint ventures.

At one time, three European producers of RMs:

1) BAS, Bureau of Analysed Samples of UK,
2) BAM, Bundesanstalt fur Materialprufung, of West Germany, and
3) IRSID, Institut des Recherches de la Siderurgie Française of France,

each prepared a wide range of similar iron and steel RMs for national use. Since the early 1970's, these three agencies have cooperated in the production of similar RMs for the European Coal and Steel Community, ECSC. These are called "Euro-standards". At first, the original "national" RMs of each agency were accepted as interim Euro-standards and it was agreed that an agency would not prepare replacement samples should similar RMs already be available from one of the other two producers. At present, each of these agencies produces RMs for ECSC using a consensus approach involving laboratories from at least four countries.

The cooperation between NBS and BNM, the French National Bureau of Metrology, is a second such example. They have exchanged a series of gas RMs used for environmental monitoring, and analyses were performed by both agencies to verify the certifications. A similar program is currently underway for a set of RMs for octane-rating. NBS has also been quite influential in establishing a RM program presently practised in Brazil by the Institute for Technical Research in Sao Paulo.

The existence of agencies such as BCR, IAEA, and WHO is in itself a reflection of the perceived need for international cooperation in the production of RMs. The availability of an international RM avoids the wasteful duplication of producing several similar national RMs. National RMs are still prerequisite where a uniqueness or special property is to be characterized.

The most prominent and important example of cooperation between the RM producing agencies of the world is REMCO, the Council Committee on RMs of ISO. The first meeting to consider international action on issues relating to the production, distribution and use of RMs was held in 1969. Even then, there was perceived to be a need for the collection of information on RMs that was not always readily available, and to make known such information in a more convenient form. This entailed making both producers and users more aware of the importance of RMs, how best they are used, what RMs are available and needed, and how to avoid unnecessary duplication of effort. The need for an international directing and controlling body to help achieve these goals in a direct way was perceived.

Ultimately REMCO was established in 1975 under the auspices of ISO to carry out this information function. Its basic function is the collection of information on type and source of RMs, its critical evaluation, and its wide-spread dissemination within ISO and the international scientific community. The importance of REMCO is clearly illustrated by the fact that 24 representatives from 14 nations, BCR, IAEA and IFCC, the International Federation of Clinical Chemists, attended the meeting in September 1982.

The primary long-term goals of REMCO are to:

(1) provide guidance to ISO technical committees concerning the production, certification and use of RMs, and
(2) enhance the production, distribution and utilization of RMs throughout the world.

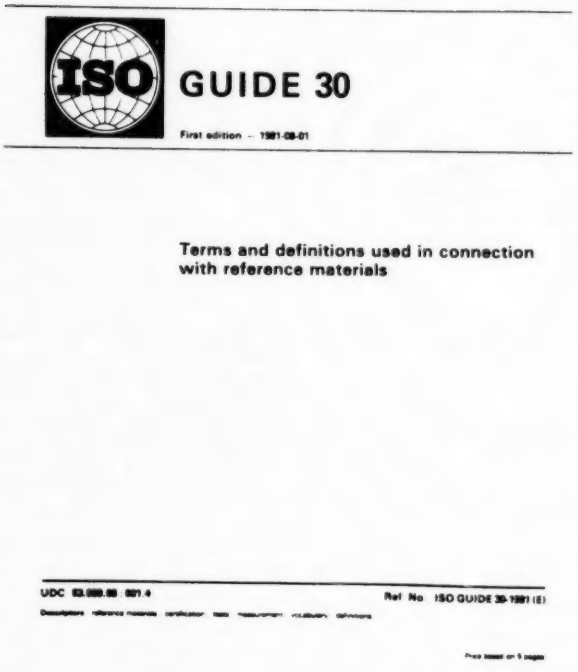
The REMCO work program can be described in terms of the following three sub-objectives:

REMCO PROGRAM

Sub-objectives	Tasks
1. Use	(a) Terms and definitions (b) Role of RMs in the measurement system (c) Role of RMs in ISO Standards (d) Review of ISO standards
2. Needs and Availability	(a) Sources of RMs (b) RMs in current and planned production (c) Identification of needs for new RMs (d) Indexing code and data bank
3. Production and Certification	(a) Principles of certification (b) Contents of certificates (c) Processing and statistical analysis of data for the assignment of a certified value

Also shown are the tasks being carried out or planned by REMCO. These are undertaken, wherever appropriate, in collaboration with ISO Working Groups or Technical Committees; IEC, the International Electrotechnical Commission; IAEA, the International Atomic Energy Agency; IUPAC, the International Union for Pure and Applied Chemistry; and WHO, the World Health organization. The outputs of the tasks are ISO Reviews, Guides and other information documents. A measure of the achievement to meet its objectives is the apparent influence that REMCO seems to exert on users and producers of RMs. The impact of REMCO should not be evaluated only in terms of the number of published documents but also of its role in enhancing the production, certification and distribution of RMs on a world-wide basis, in assuring greater uniformity of practices among RM producers and users, and in assisting developing countries in improving their RM technology.

I will now discuss a few of the outputs of REMCO. ISO Guide 30 "Terms and Definitions Used in Connection With RMs" was prepared to help



ISO GUIDE 30

First edition – 1981-08-01

Terms and definitions used in connection with reference materials

UDC [illegible] Ref No. ISO GUIDE 30-1981 (E)

ensure greater unformity in the use of terminology by different organizations in the world. It is not exhaustive but rather is concerned only with terms not yet defined by other ISO Committees or OIML, the International Organization for Legal Metrology. It is also intended to facilitate the preparation and comprehension of Certificates of Analysis by producer and user alike.

Certificates of Analysis issued with RMs vary considerably, and not only because of the varying nature of the RM. However, even certificates for similar RMs can vary from a bare statement of the certified values to a lengthy document containing detailed information. Some producers do not issue certificates at all but issue a detailed document that is sometimes not readily available. In order to bring about uniformity in Certificates of Analysis, REMCO has issued ISO Guide 31 "Contents of Certificates of RMs". It is

GUIDE 31

First edition – 1981-08-15

Contents of certificates of reference materials

UDC 53.089.68 : 381.622 Ref. No. ISO GUIDE 31-1981 (E)

Descriptors: reference materials, certification, documents, contents list.

Price based on 8 pages

DIRECTORY
of certified reference materials

RÉPERTOIRE
des matériaux de référence certifiés

First edition
Première édition
1982

intended to help producers prepare clear and concise certificates, which, while maintaining the essential character of a certificate, should help to provide all the information needed by the user of RM. The Certificates of Analysis issued by CCRMP do not follow the REMCO guidelines in a strict fashion mainly because much of the information suggested for a RM is already given in the appropriate CANMET Report on that RM and is available on request at no charge.

The most significant documentary output of REMCO to date, at least in my opinion, is the "ISO Directory of Certified RMs" which is the result of several years' work. The information therein was submitted on a voluntary basis by RM producers and it is believed to be essentially complete for the RMs of the western world. RMs have been classified into 17 types:

*Geology
Physical Chemistry
*Nuclear/Radiochemistry
Environmental
*Non-ferrous Metals
Ferrous Metals
Plastics, Rubbers
Glasses, Ceramics, Refractories
Biological, Botanical, Foods
Biomedical and Pharmaceutical
Clinical Chemistry
Paper
Petroleum
Chemicals-inorganic
Chemicals-organic
Technological and Engineering
Physics and Metrology

The types marked with an asterisk are offered by CCRMP.

The next slide shows the nature of the information in this directory. As you can see, actual descriptions of RMs are not given; this remains the function of the catalogue of each RM producer. The information in the directory does

Category A : Geology
Domaine A : Géologie

Table 1
Tableau 1

Code	Supply code Code fournisseur	CRM available MRC disponibles	Suggested uses Usages proposés
A 1	48	17 various ores certified for chemical composition of major and minor constituents (Sb, Co, Mo, Au, Fe, Mo, etc.); 9 uranium and tungsten ores; 3 rocks (syenite and gabbro); sulphide bearing ultramafic rocks; 4 soils	Calibration of instruments and control or checking of methods used for analysis of ores, rocks, other geological materials
		17 minerais divers certifiés pour composition chimique d'éléments majeurs et mineurs; (Sb, Co, Mo, Au, Fe, Mo, etc.); 9 minerais d'uranium et de tungstène; 3 roches (syénite et gabbro); 2 roches ultramafiques contenant des sulfures; 4 sols	Etalonnage d'instruments et examen ou contrôle de méthodes d'analyse de minerais, de roches et d'autres matériaux géologiques
A 2	66, 147	36 geological materials, e.g., basalt, bauxite, granite, iron ores (certified for major, minor, and trace constituents as appropriate)	Calibration of instruments and checking or control of methods used in analysis of ores and other geological materials
		36 matériaux géologiques, basalte, bauxite, granite, minerais de fer (certifiés pour éléments majeurs, mineurs et oligo-éléments, s'il y a lieu)	Etalonnage d'instruments et contrôle ou examen de méthodes d'analyse de minerais et d'autres matériaux géologiques
A 3	159	Series of 4 U_3O_8 containing ores (Certified for uranium concentrations in range from 0.04 to 0.5 % of U_3O_8)	Intended for use in uranium prospecting; cautioned for use as counting standard
		Série de 4 minerais contenant U_3O_8 (Certifiés pour les concentrations d'uranium de 0.04 à 0.5 % de U_3O_8)	Prévu pour la prospection d'uranium; usage recommandé comme étalon de comptage
A 4	129, 219	(A) Granodiorite, basalt (B) feldspar, clay (3); alabaster (2)	(A) and (B) Calibration of instruments and control or checking of methods used for analysis of rocks and other geological materials
		(A) Granodiorite, basalte (B) feldspath, argile (3); albâtre (2)	(A) et (B) Etalonnage d'instruments et examen ou contrôle de méthodes d'analyse de roches et d'autres matériaux géologiques
A 5	282	Granite, syenite, lujavrite, norite, pyroxenite, dunite, hematite and magnetite, Platinum, chromium, iron ores, ferrochromium	Instrument calibration; test new methods of analysis; RM for purchase and sale of ores NOTE - Detailed reports of CRM analytical work available from 282
		Granite, syénite, lujavrite, norite, pyroxénite, dunite, hématite et magnétite, Minerais de platine, de chrome, de fer, ferrochrome	Etalonnage d'instruments, essai de nouvelles méthodes d'analyse, MR pour achat et vente de minerais NOTE - Rapports détaillés des travaux analytiques sur les MRC disponibles au 282

Supplier code numbers and addresses of CRM suppliers

Numéros de codes et adresses des fournisseurs de MRC

Table 2
Tableau 2

Supplier code number N° code fournisseur	CRM suppliers and addresses Fournisseurs de MRC et adresses
6	**Airco Industrial Gases** 575 Mountain Avenue Murray Hill, N.J. 07974 USA
8	**Air Liquide** Direction Gaz Division Scientifique 75, quai d'Orsay 75321 Paris Cedex 07 FRANCE
9	**Air Products Ltd** Special Prods. Dept. Weston Rd. Crewe Cheshire CW1 6DF UNITED KINGDOM/ROYAUME-UNI
10	**Alpha Analytical Laboratories, Inc.** 57 Freeman Street Newark, N.J. 07105 USA
12	**Aluminium Pechiney** 23bis, rue Balzac 75380 Paris Cedex 08 FRANCE
13	**Analytica AB** Box 6 S-19121 Sollentuna SWEDEN/SUEDE
14	**American Tyna Culture Collection** 12301 Parklawn Drive Rockville, MD 20852 USA
15	**Anglia Chemical Products Ltd** 138 St. Paul's Rd. London N1 2LP UNITED KINGDOM/ROYAUME-UNI
16	**Angstrom, Inc.** P.O. Box 249 Berkley, MI 48111 USA
17	**API Standard Reference Materials** Attention: A. J. Streiff Carnegie Mellon University Schenley Park Pittsburgh, PA 15213 USA
18	**Asociación de Investigación de la Industria Gráfica** c/o Pedro Martinez Artola No. 4-1 Bilbao 12 SPAIN/ESPAGNE
19	**Amersham Corporation** 2636 S. Clearbrook Drive Arlington Heights, IL 60005 USA
21	**BDH Chemicals Ltd** Poole Dorset BH12 4NN UNITED KINGDOM/ROYAUME-UNI
24	**Biomérieux** Chemin de l'Orme Marcy L'Etoile 69280 Charbonnières-Les-Bains FRANCE
27	**Biotrol** 1 rue du Fort 75740 Paris Cedex 03 FRANCE
30	**BNF Metals Technology Centre** Grove Laboratories Denchworth Road Wantage Oxfordshire UNITED KINGDOM/ROYAUME-UNI
31	**Brammer Standard Company, Inc.** 5407 Fountainbridge Lane Houston, TX 77069 USA

however give the user an indication of possible sources for RMs of interest to him. Before the publication of this directory, much of this information was available only by word of mouth. CCRMP often receives requests for information on the nature and sources of particular types of RMs that it does not itself offer and the directory has proven very useful for this purpose in those instances where the catalogues of RMs from various sources that CCRMP possesses have not been helpful or are not available. I should state at this point that RM producers in general are quite willing to provide information on potential sources of appropriate RMs to users. Indeed CCRMP considers this to be one of its duties.

As in the case with many documents describing the current state, the Directory of Certified RMs must be updated on a periodic basis. REMCO has accordingly prepared a compendium entitled "New Certified RMs in Current and Planned Production" which was approved for general distribution last September. The information therein will eventually be incorporated into a revised Directory of Certified RMs.

For those who may be interested, ISO Guides 30 and 31 and REMCO Directory of Certified RMs may be purchased from

Standards Council of Canada
2000 Argentia Road, Suite 2-401
Mississauga, Ontario
L5N 1V8

To complete this description of REMCO, I would like to mention that the preparation of a composite guide on the role, certification and use of RMs is presently underway. Canada, through CCRMP, was responsible for the section on the "Processing and Statistical Analysis for the Assignment of a Certified Value from Data from an Interlaboratory Program". Much of this contribution to REMCO has been discussed in the previous presentations.